## REMARKS/ARGUMENTS

Claims 6-25 are active in the case.

The Examiner's allowance of Claims 10, 11, and 19-25 is appreciated.

Claim 12 has been amended to delete the phrase "the a=0 and". No new matter has been added into the amended claim.

The rejection of Claim 6 under 35 U.S.C. § 112, second paragraph, as being indefinite for lacking antecedent basis for "a=0" is traversed.

It appears that the Examiner intended to refer to Claim 12, which contains the above limitation. With the cancellation of the above phrase from Claim 12 this rejection is now moot.

The rejection of Claims 6-9 and 12-18 under 35 U.S.C. § 103(a) as unpatentable over 103(a) as unpatentable over Yu is traversed.

Yu discloses a polyether macromer having a styryl group and a hydroxy group at the terminal positions. Polymerization to form the polyether macromer is disclosed in Yu as being carried out with the use of specific acid catalysts to produce polyether macromers with a molecular number up to about 10,000 (see column 5, lines 20-56).

Therefore, the conventional catalyst employed by Yu could not possibly produce a polymerization degree of 150 or more on the average, as claimed in Claim 6. To support this argument Applicants submit for the Examiner's consideration the attached publication, Polymer Chemistry 17, 179, pages 175-182 (1960) and a translation thereof. It is clear from the results set forth in Table 3 of the publication that acidic catalysts like those of Yu, specifically including tin tetrachloride and a borontrifluoride ether complex, which are set forth in Yu in column 5, lines 48-49, cannot produce a polymerization degree of 150 or more on the average. Therefore, since Yu fails to disclose a process which will produce a

polyether having the high degree of polymerization of the present claims, <u>Yu</u> fails to teach or

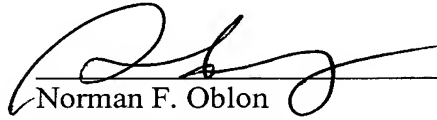suggest the claimed invention and the claims distinguish over the reference.

It is submitted that Claims 6-25 are allowable and such action is respectfully

requested.

Respectfully submitted,

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〔33〕　　　　高分子化学　第17巻　第179号　(1960)　　　　　　175

# 〔37〕　グリジジルエーテルおよびグリセリルエーテルを中間体とする界面活性剤の研究

## 第2報　アルキルグリシジルエーテルよりブロックポリマー型非イオン性界面活性剤の合成

桑　村　常　彦*

要　旨　アルキル鎖長 $C_2 \sim C_{12}$ のアルキルグリシジルエーテルを，アルカリあるいは酸性触媒により重合させ，平均重合度 4~30 の低重合物を得た。低起泡性の非イオン活性剤を得る目的で，これらに酸化エチレンを逐次付加して，$HO(CH_2CH_2O)_{\overline{y}}(CHCH_2O)_{\overline{x}}(CH_2CH_2O)_{\overline{z}}H$ のような一般式のポリグリシジルエーテルを疎水ベースとするブロックポリマーを合成した。ポリオキシエチレン含量 55% 以上のブロックポリマーのうち，疎水ベースの分子量 2500 以下で，かつ側鎖アルキル基が比較的短鎖のものは，一般に水によく溶解または分散して相当の表面張力低下能を有し，かつプロピレンオキサイド－エチレンオキサイド型活性剤に近い低起泡性を示した。疎水ベースのアルキル鎖長大で分子量が 2500~3000 以上の場合は，酸化エチレン高付加体でも水溶性に乏しく，その表面活性も劣っているが，水中で著しく膨潤する。
$CH_2OR$

## 1.　緒　　言

ブロックポリマー型非イオン活性剤としては，ポリプロピレンオキサイドを疎水ベース，ポリオキシエチレンを親水基とした製品について，すでに Vaughn らの詳しい研究[1]があり，また低起泡性を特徴とする新型活性剤として市販されてもいる。また古川ら[2]はフェニルグリシジルエーテルポリマーと酸化エチレンから水溶性のブロックポリマーを得たが，その表面活性にはみるべきものがないとしている。しかしアルキルグリシジルエーテル (AGE と略称する) からの誘導については報告がない。Vaughn らの研究とは別個に，以前筆者がエポキシ化合物の重合を取り扱った際，エチル GE のポリマーが低重合物でも水に不溶で，これに酸化エチレンを逐次付加することにより，水溶性のかなり表面活性を示す物質が得られることを知り，AGE ポリマーが界面活性剤の

疎水ベースとなることを認めた。

一方 AGE は現在工業的製造および利用がほとんど行なわれていないが，脂肪族アルコールとエピクロロヒドリンから比較的容易に得られるものであり，その利用途の広いことについても前報に述べたところである[3]。ここでは AGE の活性剤への利用研究の一環として，これらから導かれるブロックポリマーの構造（特に疎水基主鎖の重合度，側鎖アルキル鎖長）と諸性質の関係について知見を得る目的で，数種の AGE につき重合を試み，さらに酸化エチレン付加生成物を得て，これらの水溶性，表面活性などにつき概略の検討を行なった。

## 2.　実験とその結果

### 2.1　AGE の重合

重合に用いた AGE はすべて前報[3]の方法により合成したもので，その種類と性状を第1表に示す。フェニル

第 1 表　原料アルキルグリシジルエーテルの性状

| ROCH₂-CH-CH₂ (O) R | 沸　点 (°C/mmHg) | オキシラン酸素含量(%)[*1] | | 比　重 $d_4^{20}$ | 屈折率 $n_D^{20}$ |
|---|---|---|---|---|---|
| | | 実　測 | 計　算 | | |
| $C_2H_5-$ | 126.5~127.5 | 15.3 | 15.6 | 0.9302 | 1.4035 |
| $n-C_4H_9-$ | 74~75/26 | 12.1 | 12.3 | 0.9041 | 1.4198 |
| $i-C_5H_{11}-$ | 72~73/14 | 10.9 | 11.1 | 0.8987 | 1.4200 |
| 2-エチルヘキシル | 89.5~90.5/2 | 8.38 | 8.51 | 0.8862 | 1.4305 |
| $n-C_8H_{17}-$ | 140~141.5/30 | 8.45 | 8.51 | 0.8787 | 1.4301 |
| $n-C_{12}H_{25}-$[*2] | 119~120/1.2 | 6.44 | 6.61 | 0.8688 | 1.4391 |

[*1]　エーテル-HCl 法 ｝ を用いた。(前報[3]参照)　[*1]　融点 11.8~12.3°C (補正値)
　　　氷酢酸-HBr 法 ｝

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4/

GE について重合の報告はあるが[2],[4], AGE に関しては見出されないので, エポキシ化合物の重合に一般に用いられているアルカリ触媒と無水四塩化スズ, 三フッ化ホウ素などの酸性触媒を用いて以下のごとく行なった。

2.1.1　アルカリ触媒による重合

a.　常圧無かきまぜ法　遮流冷却器, 防湿管をつけたフラスコ中で 2～5% の KOH 粉末を添加したモノマーを油浴により加熱する。100℃付近で急激な反応が起り, 著しい反応熱の発生とともに内容物は黄褐ないし黒褐色となり, 粘度を増してくる。さらに長時間加熱を続けて粘度増加が見られなくなって反応を終る。この方法では特に原料モノマーの純度が高い場合, 反応開始時の温度の制御は困難である。

b.　常圧滴下かきまぜ法　防湿管, かきまぜ器, 滴下漏斗 および温度計を備えた三ツ口フラスコ中に少量(使用全量の 1/5 以下)のモノマーと KOH 粉末を入れ,

よくかきまぜつつ徐々に加熱する。発熱の始まったときに加熱浴を去り, 残部のモノマーをきわめて徐々に(約1時間以上)滴下して, 内容物温度を一定に保つよう調節する。この方法によればブチル以上の長鎖モノマーの場合には温度制御が可能であった。

c.　封管法　モノマーと触媒を封管に入れ, 一定温度の油浴中で長時間加温し, 時おり激しくふりまぜて沈降した触媒を分散させる。

以上のようなアルカリ触媒法で得られるポリマーはいずれも黒褐色を呈しているが, ベンゼン溶液中で活性白土, 活性炭を交互に用い脱色することにより, きわめてわずかな損失量(2%以下)で淡黄色ないし淡褐色となる。精製ポリマーの平均重合度は氷点降下法(ベンゼン中), ラスト法および OH% 測定法[5]により求めたが, いずれの方法によってもほぼ同じ結果を与えた。以上の結果を第2表に示す。表から主要な実験結果をあげてみる

第2表　塩基性触媒による AGE の重合

| モノマー R | 方法 | 触媒 種類 | 使用量 (%) | 加熱温度 (℃) | 加熱時間 (hr) | 収率 (%) | 平均分子量 測定値(重合度) | 測定法* | 備考 | 合成番号 |
|---|---|---|---|---|---|---|---|---|---|---|
| C₂H₅- | (a) | KOH粉末 | 5 | 110～140 | 30 | 85 | 805(8) / 815(8) | R / F | 淡黄色高粘性液体 | E-8B |
| | | トリエチルアミン | 3 | 80～140 | 50 | — | — | — | 重合物得られず | — |
| n-C₄H₉- | | KOH粉末 | 5 | 120～140 / 150～160 | 6 / 15 | 75 | 820(6.3) | R | 淡褐色高粘性液体 | B-6B |
| n-C₄H₉- | (b) | KOH粉末 | 5 | 140～150(滴下) / 150～180(かきまぜ) | 0.5 / 10 | 86 | 788(4.2) | R | 淡橙褐色　〃 | B-4B |
| n-C₈H₁₇- | | 〃 | 〃 | 140～145(滴下) / 150～160(かきまぜ) | 1 / 12 | 88 | 1323(7.1) | 〃 | 淡褐色　〃 | O-7B |
| n-C₁₂H₂₅- | | 〃 | 〃 | 160～165(滴下) / 165～175(かきまぜ) | 1 / 7 | 85 | 850(3.5) | 〃 | 淡黄色ワックス 融点 16～18℃ | D-3.5B |
| C₃H₅- | | KOH粉末 | 3.3 | 60～65 | 120 | 80 | 1960(19) | R | 褐色高粘性液体 | E-19B |
| | | 〃 | 3 | 95～100 | 50 | 84 | 1330(13) | 〃 | 〃 | E-13B |
| | | 〃 | 〃 | 120～130 | 26 | 90 | 1110(11) | 〃 | 黒褐色 | E-11B |
| | | トリエチルアミン | | 100～120 | 50 | — | — | — | 1ヵ年以上放置したが重合せず | — |
| | (c) | KOH粉末 | 5 | 60～65 | 120 | 85 | 2800(22) | F | 淡黄色高粘性液体 | B-22B |
| | | 〃 | | 95～100 | 50 | 79 | 3030(23) | 〃 | 淡橙色　〃 | B-23B |
| n-C₄H₉- | | 〃 | 10 | 〃 | 50 | 88 | 4010(31) / 4350(33) | F / OH | 淡褐色　〃 | B-31B |
| | | 〃 | 5 | 120～130 | 25 | 84 | 2200(17) | F | 黒褐色　〃 | B-17B |
| i-C₅H₁₁- | | 〃 | | 57～60 | 150 | 93 | 2880(20) | 〃 | 淡黄色 | A-20B |
| 2-エチルヘキシル | | 〃 | 1 | 120～130 | 200 | — | — | — | 6カ月以上放置したが重合せず | — |
| n-C₈H₁₇- | | 〃 | | 〃 | 100 | 94 | 4600(25) | R | 淡褐色高粘性液体 | O-25B |
| n-C₁₂H₂₅- | | 〃 | | 〃 | | 90 | 2660(11) / 2710(11) | R / OH | 淡黄色ワックス 融点 22.5～24.5℃ | D-11B |

\* R: ラスト法　F: ベンゼンを溶媒とする氷点降下法　OH: OH% 測定法。

と，(1) トリエチルアミンのごとき3級アミン塩基は触媒効果が認められず，この点は酸化エチレンの重合の場合と異なる。(2) 低重合度のポリマーを得るには常圧下の反応が適しており，特に(b)法によりやや高い温度で重合を行なえば短時間で高収率の低重合物を得る。(3) やや高い重合度のポリマーを得るには封管法が適しており，この場合反応温度の低いほど長時間を要するが，より高重合物を与える。(4) 一般にアルキル基鎖長の差異による重合性の変化は，顕著には認められないが，2-エチルヘキシルモノマーのみは新鮮な粉末 KOH 触媒を用いて封管重合を3回試みたにもかかわらず，常にモノマーが定量的に回収された。(5) KOH 粉末を触媒とする重合では一般に長時間を要するが，重合条件の適当な選択により各種のモノマーから平均重合度4〜30のポリマーを高収率で得る。

2.1.2 酸性触媒による重合

a. 防湿管をつけた試験管中にモノマーを入れ0°C以下に冷却しておく。ここへ 1〜10% の無水四塩化スズを含む無水リグロインを少量加えて放置する。

b. 温度計，滴下漏斗，防湿管およびかきまぜ器を備えた三ツ口フラスコ中にモノマーと同量以上の無水溶媒およびモノマーに対して 1〜5% の触媒を封入したアンプルを入れ，かきまぜ器の回転によりアンプルを砕き触媒を分散させる。内容物を −10〜−5°C に冷却してから，モノマーを温度が 5°C 以下に保たれるように留意しつつ徐々に滴下する。その後さらに 0°C 付近でしばらくかきまぜを続ける。

c. a.とほぼ同様な割合でモノマーに触媒溶液を加え，封管中で 80〜100°C に加温する。

これらの方法で得た生成物をエーテルに溶解し，高濃度(10% 以上)の NaOH 水溶液と振って触媒の分解を行ない(低濃度のアルカリを用いると乳化が起りエーテル層の分離を困難にする)2液層を分離する。エーテル層を水洗，乾燥後溶媒を留去してポリマーを得る。反応結果をまとめて第3表に示す。

実験結果を要約すると，本法によれば一般に収率，重合度がアルカリ触媒法の場合に比べやや低いが，ポリマーの着色はきわめて少なくて脱色操作を要しない。また反応を要する時間も短い。$BF_3(C_2H_5)_2O$ を触媒として得たポリマーの平均重合度は測定法によって異なり，OH%法では氷点降下法での約2倍に近い結果を与える。おそらくポリマー端に触媒断片(エチル基)が結合しているためかと思われる[6]。無水四塩化スズを触媒とする場合にも，OH% 測定法による重合度測定値がやや大きい傾向はあるが，その差異はあまり大きくない。

両触媒法を通じて，得られるポリマーはいずれも水に不溶，ベンゼン，ピリジン，エーテル，ジオキサンなどに易溶，アルコール，アセトンなどには低重合物または長鎖のアルキル基をもつポリマーが易溶であるが，他のポリマーでは冷時難溶のものが多い。ポリマーの粘度は一般に高いが，その温度依存性は少ないようである。側鎖アルキル基の大きいポリマーほど，同一温度での粘性はやや低くなる傾向がある。

2.2 AGE ポリマーへの酸化エチレン付加

2.2.1 反応方法および経過

反応方法としてはカセイカリ粉末を触媒とする常圧下

第3表 酸性触媒による AGE の重合

| モノマー R | 方法 | 重合条件 触媒 種類 | 使用量[*1] (g) | 溶媒 種類 | 使用量[*1] (g) | 温度 (°C) | 時間 (hr) | 収率 (%) | 精製ポリマー 平均分子量 測定値(重合度) | 測定法[*3] | 備考 | 合成番号 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| n-$C_4H_9$- | (a) | $SnCl_4$ | 0.02 | リグロイン | 1 | 0〜10 | 10 | <5 | — | — | — | — |
| $C_2H_5$- | | $SnCl_4$ | 1.10 | 石油エーテル | 40 | -2〜5 | 4 | 59 | 650(6.4) | F | 無色粘性液体 | E-6A |
| n-$C_4H_9$- | (b) | 〃 | 0.75 | リグロイン | 30 | -2〜4 | 3.5 | 81 | 780(6.0) / 1020(8.0) | R / OH | 〃 | B-6A |
| n-$C_4H_9$- | | $BF_3(C_2H_5)_2O$[*2] | 0.25 | 石油エーテル | 〃 | -10〜-5 | 6 | 50 | 1080(8) / 1870(14) | F / OH | 〃 | B-8A |
| n-$C_8H_{17}$- | | $SnCl_4$ | 1.20 | リグロイン | 40 | 0〜3 | 5 | 77 | 1310(7) | R | 微黄色 〃 | O-7A |
| n-$C_8H_{17}$- | | $SnCl_4$ | 0.15 | リグロイン | 5 | 80〜100 | 20 | 32 | 560(3) | R | 淡黄色高粘性液体 | O-3A |
| n-$C_{12}H_{25}$- | (c) | 〃 | 0.15 | 〃 | 〃 | 〃 | 〃 | 40 | 1005(4) | 〃 | 淡黄色ワックス 融点 17〜19°C | D-4A |

[*1] いずれもモノマー 25g に対する使用量
[*2] Eastman Kodack 製品を1回蒸留して使用 沸点 124.5〜126°C
[*3] R: ラスト法，F: 氷点降下法(溶媒はベンゼン)，OH: OH% 測定法

第4表　ポリグリシジルエーテルへの酸化エチレン付加

| 合成番号 | 疎水ベース | | | 反応条件 | | | 生成物 | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | 構　造 | $\bar{n}$ | 平均分子量 | 触媒量 (%) | 温度 (°C) | 時間 (hr) | 酸化エチレン付加量(%)[*1] | 基本モル比 EO/GE[*2] | 外　観 | 水溶性[*3] |
| S-12 (61) | H-(CH₂)ₙ-O- | 12 | 185 | 1 | 135~140 | 5 | 61 | 6.6 | 淡黄色半固体 | 透明に可溶 |
| P-20 (55) | (CH₃ / -CH-CH₂-O-)ₙ | 20 | 1120 | 3 | 130~135 | 5 | 55 | 1.6 | 淡灰色半固体 | 透明に可溶 |
| P-20 (76) | | | | " | " | 6 | 76 | 4.2 | 淡褐色ワックス | " |
| E-8B (76) | (CH₂OC₂H₅ / -CH-CH₂-O-)ₙ | 8 | 810 | 3 | 130~135 | 4 | 76 | 7.1 | 淡黄色半固体 | 透明に可溶 |
| E-13B (59) | | 13 | 1330 | 2 | 135~140 | 6 | 59 | 3.3 | 淡橙色 " | " |
| R-6B (52) | (CH₂On-C₄H₉ / -CH-CH₂-O-)ₙ | 6.3 | 820 | 3 | 120~130 | 10 | 52 | 3.2 | 黄色半固体 | 白濁分散 |
| B-6A (57) | | 6 | 780 | 3 | 130~135 | 12 | 57 | 4.0 | " | 薄白濁 大部分溶解 |
| B-17B (63) | | 17 | 2220 | 5 | 140~150 | 8 | 63 | 5.0 | 淡黄色 粘性ワックス | 白濁分散 |
| A-20B (40) | (CH₂Oi-C₅H₁₁ / -CH-CH₂-O-)ₙ | 20 | 2880 | 2 | 135~140 | 9 | 40 | 2.2 | 淡褐色半固体 | 難溶 わずかに分散 |
| A-20B (76) | | | | 4 | 140~145 | 15 | 76 | 10.5 | 淡灰色 ワックス | 分散 わずかに可溶 |
| O-7A (64) | (CH₂On-C₈H₁₇ / -CH-CH₂-O-)ₙ | 7.0 | 1310 | 2 | 130~135 | 17 | 64 | 7.5 | 黄白色 ワックス | 薄白濁分散 |
| O-7B (71) | | 7.1 | 1323 | 1 | 150~160 | 8 | 71 | 10.3 | " | " |
| D-3.5B (54) | (CH₂On-C₁₂H₂₅ / -CH-CH₂-O-)ₙ | 3.5 | 850 | 1 | 150~160 | 5 | 54 | 6.5 | 淡褐色 粘性ワックス | 白濁分散 |
| D-3.5B (74) | | | | " | " | 6 | 74 | 15.7 | 黄色ワックス | 薄白濁分散 |
| D-4A (74) | | 4.0 | 1005 | | 135~140 | 10 | 74 | | " | " |
| D-11B (42) | | 11 | 2660 | 3 | 140~145 | 8 | 42 | 4.0 | 黄白色半固体 | 不溶 |
| D-11B (68) | | | | " | " | 10 | 68 | 11.7 | 黄白色 ワックス | 難溶 わずかに分散 |

*1 反応増量より求めた生成物中の酸化エチレン結合重量
*2 EO: 酸化エチレン. GE: グリシジルエーテル
*3 水に対し0.5%の生成物を加えよくふりまぜたときの外観

酸化エチレン吹込法[7]によった。反応に先立ち装置内空気はN₂ガスまたはアルゴンガスで置換した。比較的低分子量のAGEポリマーの場合には酸化エチレンの吸収が順調で、4～8時間以内に予定の反応増量に達する。しかし高分子量あるいは長鎖アルキル基を含むAGEポリマーの場合は、反応系の粘度、末端ヒドロキシル基濃度の低いことなどに原因すると思われるが、一般に吸収不順で相当長時間を要する場合が多かった。

2.2.2　反応結果(主として生成物の水溶性)

ポリAGE系ブロックポリマーの他に、比較物質として高純度のn-ドデカノールおよびポリプロピレンオキサイド(Dow Chem. Co製品, 無色粘性液体, $\overline{MW}_n$: 1120)に同様の方法で酸化エチレン付加を行なった試料をも合成した。これらの反応結果を第4表にまとめてある。表示してないが数種の生成物について分子量測定を行なった結果では、いずれも原料ポリマーより高く反応増量に基く計算値より一般にかなり低い値を得た。特に高分子量の原料ポリマーを用いたときにはその傾向が著しいので、疎水ベースに結合していないポリグリコールの副生量は一般の非イオン活性剤に比べやや多いと推測される。しかし単にAGEポリマーとポリグリコールを混合加熱しただけでは水溶性ないし分散性の生成物は得られない。反応生成物は少なくともある程度以上のポリグリコール鎖と結合した予期のごときブロックポリマーを主体とするものと思われる。第4表の結果を要約すると、(1) 疎水ベースの分子量2000以下で、酸化エチレン付加量55～60%以上の場合は、一般の水溶性ないし高分散性の生成物を得るが、疎水ベースが高分子量のと

きは酸化エチレン高付加体でもかろうじて分散あるいは難溶である。しかし，たとえば表中の A-20B(40) のごとき高分子量疎水ベースに酸化エチレンを低度付加した難溶性生成物でも，水中で徐々に膨潤する性質があり，乳化分散に対する保護コロイドとしての応用も条件により可能と思われる。(2) ほぼ同程度の酸化エチレン付加量でかつ疎水ベースの分子量 2000 以下の生成物においても，側鎖アルキル基が長鎖のものほど水溶性の低下する傾向があり，AGE ポリマーの hydrophobic な性質はその重合度のみでなくアルキル鎖長に著しく依存している。したがってこれらブロックポリマーの水溶性は疎水ベースの重合度よりもむしろ分子量，アルキル鎖長および酸化エチレン鎖長により規定されると思われる。(3) 原料ポリマーの重合に，アルカリ，酸性いずれの触媒を用いたかは，最終生成物の水溶性にあまり影響していない。

### 2.3　ブロックポリマー水溶液の性質

#### 2.3.1　曇点および粘度

水溶性の生成物では通常の非イオン活性剤と同様に比較的シャープな曇点を示す。二，三の測定例を 第 5 表に示す。しかし曇点と濃度あるいは推定される HLB 値と

第 5 表　ブロックポリマー水溶液の曇点

| 濃度 (%) 合成番号 | 曇　　　　点　(°C) | | |
|---|---|---|---|
| | 3 | 1 | 0.5 |
| S-12　(61) | 46.8 | 48.0 | 49.7 |
| P-20　(55) | 77.1 | 76.0 | 75.4 |
| E- 8 B (76) | 86.2 | 83.8 | — |
| E-13 B (59) | 94.1 | 94.2 | 95.2 |

の関係に規則性がなく，ブロックポリマー型非イオン活性剤では，親水基長および疎水ベースの重合度に分布があるほか副生ポリグリコール量が多く，かつその生成量が一定しないなど曇点に関係する因子がきわめて複雑なので，曇点を特性値として利用することは困難である。

水に透明に溶解する二，三の試料について，オストワルド型粘度計（蒸留水の流下時間 200～300 sec）を用い，25±0.05°C 恒温槽中で濃度 5 g/100 cc 以下の希薄水溶液粘度を測定した。濃度とReduced Viscosity ($\eta_{sp}/C$) の関係を第 1 図に示す。試料純度に問題があるので立入った論議はできないが，測定結果から明らかなことは，S-12(61) のごとき通常の（疎水基の一端のみに長鎖親水基を有する）非イオン活性剤とブロックポリマーとでは 0.5 g/100 cc 以下の低濃度範囲における粘度挙動の異なる点である。すなわち前者の関係曲線には濃度 0.1 g/100 cc
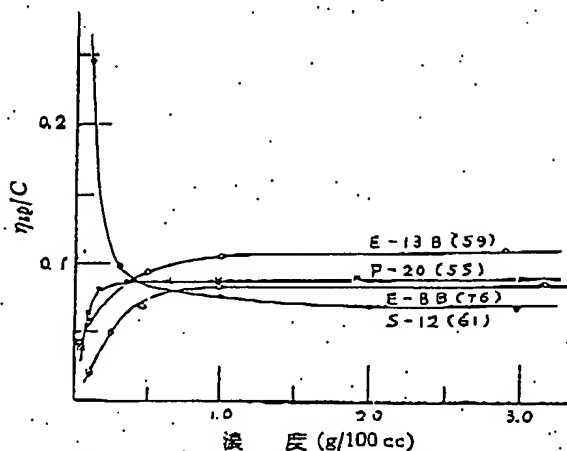


第 1 図　ブロックポリマーの希薄水溶液粘度
(25±0.05°C)

以下（この濃度以下では測定精度が疑問とされるので図示してないが）におそらく極大をもっと思われるのに対し，後者ではその傾向がない。しかし両者ともに 1.0 g/100 cc 以下のある濃度にそれぞれ明瞭な屈曲点をもち，この屈曲点濃度は次に示す表面張力-濃度曲線の屈曲点に大体対応しているので，ブロックポリマー型活性剤においても水溶液の粘度的挙動がミセル様集合体の生成に関連していると思われるが，その集合形体は通常の非イオン活性剤 (S-12(61)) に比べ生成の初期から むしろランダムコイルに近い糸マリ状をとるのではないかと推測される。屈曲点以上の濃度では，その比粘度が主として疎水ベースの分子量の大小に依存しているように思われる。

#### 2.3.2　表面張力

Du Nouy 型テンシオメーターを用い 27～29°C の室温下で測定した。まず標準型試料と AGE 系ブロックポリマーの代表例 (E-13 B (59)) の比較を 第 2 図に示す。S-12(61) のごときポリグリコールモノアルキルエーテル型に比べ，ブロックポリマー型活性剤は表面張力低下
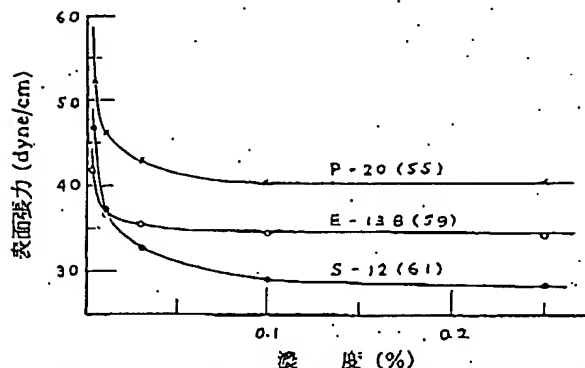


AGE 系ブロックポリマーと標準型非イオン活性剤の比較
第 2 図　表面張力-濃度曲線　(27～29°C)

能がやや劣るが，AGE系は場合によりむしろプロピレンオキサイド系よりもすぐれており，特に表面張力-濃度曲線の屈曲点，すなわち推定 cmc 濃度が低いので比較的低濃度でかなりの表面活性を示す。

AGE系ブロックポリマー中，疎水ベースの分子量 2000 以下（可溶ないし高度分散性生成物）の場合の側鎖アルキル鎖長を異にする試料の比較を第3図に示す。側
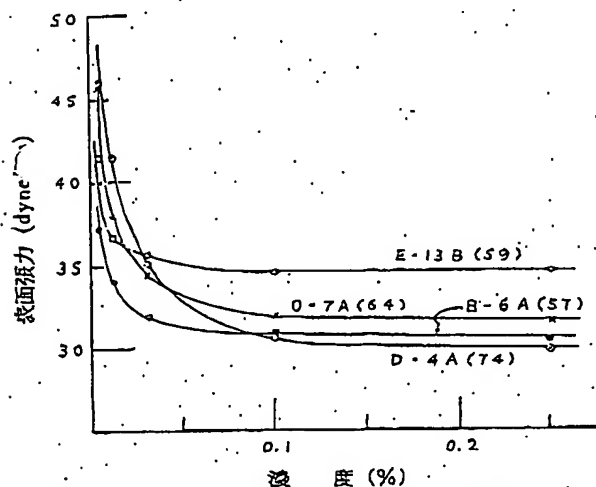


第3図　側鎖アルキル鎖長の異なる可溶性ブロックポリマーの表面張力-濃度曲線（27〜29℃）

鎖アルキル基がエチルからドデシルの間では顕著な差異とはいえないが，アルキル鎖長の大きいほど表面張力低下能がややすぐれている傾向がある。

次にブロックポリマーの表面活性に及ぼす疎水ベースの分子量の影響を第4図に示す。これらの試料は水溶性に乏しく，きわめて低濃度でしか測定に供しえないが，疎水ベース分子量の過大（2500 以上）は明らかに界面活性を著しく低下させるといえる。Bistline[8] らは α-スルホ脂肪酸の Allyl ester salt についてモノマーとポリマーの表面活性の差異を検討した結果，ポリマー（重合度約10）の表面張力低下能，湿潤性，洗浄力などが非常に劣る一方，乳化分散力が比較的良いことを認めている。活
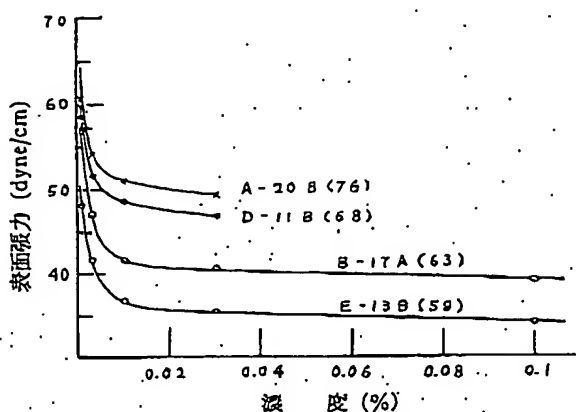


第4図　疎水ベース分子量の大きいブロックポリマーの表面張力-濃度曲線（27〜29℃）

性剤の類型としては本研究のブロックポリマーとやや異なり，同一に論ずるに問題はあるが，これらの結果はたとえ可溶性活性剤において Hydrophilic-Lyophilic-Balance が成立している場合でも，いわゆる表面活性の顕著な化合物としては，その分子量の大きさに限度があり，この限界以上ではむしろその特性が高分子的保護コロイド性に移行することを示すと考えられる。

### 2.3.3　起　泡　性

0.6 l のスチーベル型フラスコを用い 40 cc の試料液を次の条件でふりまぜ起泡させ，その泡面と液面の読みを観測した。

温度：30±1℃，試料濃度：0.25, 0.05%，ふりまぜ：試料液の入ったフラスコを恒温槽中に 15 分間置いた後取り出し，1 分間 100 回上下ふりまぜてから恒温槽に戻したときを時間 0 とする。1, 3, 5, 10 分後にそれぞれ泡面，液面の読みを取った。

結果の表示：中川の取扱[9] を準用して測定結果を処理した。その結果を第6表に示す。

$$起泡係数 (FC) = 泡容積 \times 泡化液量$$

$$泡の比容 (FV) = 泡容積 / 泡化液量$$

$$泡消率 (DFC_t) = (FC_1 - FC_t) 100 / FC_1$$

第 6 表　ブロックポリマー水溶液の起泡性

| 濃　度(%) | 0.25 | | | | 0.05 | | | |
|---|---|---|---|---|---|---|---|---|
| 試　料 | $FC_1(a)$ [*1] | $FV_3$ | $DFC_3$ | $DFC_{10}$ | $FC_1(a)$ [*1] | $FV_3$ | $DFC_3$ | $DFC_{10}$ |
| n-$C_{12}H_{25}OSO_3Na$ [*2] | 1265 (186) | 88 | 52 | 80 | 145 (35) | 13 | 44 | 75 |
| イゲポンT [*3] | 3030 (416) | 274 | 45 | 76 | 700 (70) | 34 | 61 | 78 |
| S-12 (61) | 2340 (233) | 110 | 58 | 80 | 539 (62) | 17 | 55 | 72 |
| P.-20 (55) | 66 (32) | 14 | 80 | 98 | 3 (5) | 8 | 77 | 99 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| E-13B (59) | 102 (47) | 21 | 48 | 88 | 65 (16) | 16 | 74 | 95 |
| B- 6A (57) | 120 (54) | 22 | 62 | 92 | 43 (12) | 12 | 61 | 90 |
| O- 7A (64) | 43 (18) | 15 | 75 | 94 | 5 (5) | 11 | 52 | 83 |
| D- 4A (74) | 8 (6) | 6 | 40 | 76 | 3 (4) | 8 | 58 | 82 |

*1 (a) カッコ内は実際の起泡容積 cc を示す
*2 純粋合成試料
*3 市販品

第 7 表　ブロックポリマーの温潤力 (40°C)

| 試　　料 | 沈　下　時　間　(sec) | | | | |
|---|---|---|---|---|---|
| | 0.5 % | 0.25 % | 0.1 % | 0.05 % | 0.025 % |
| n-$C_{12}H_{25}OSO_3Na$ | 5.3 | 8.6 | 36.2 | 126 | 沈下せず* |
| S-12　(61) | 4.0 | 5.2 | 13.2 | 25.2 | 73.5 |
| P-20　(55) | 28 | 87 | 315 | 沈下せず* | — |
| E-8 B (76) | 144 | 354 | 沈下せず* | — | — |
| E-13B (59) | 31.4 | 74.0 | 221 | 沈下せず* | — |
| B- 6A (57) | 460 | 沈下せず* | — | — | — |
| O- 7A (64) | 840 | 〃 | — | — | — |
| D-4A (74) | 沈下せず* | — | — | — | — |

* 20分間以内に沈下しないもの

　ブロックポリマー型の試料はいずれも，他の一般の標準型活性剤に比べ，起泡係数は著しく小，泡の比容も概して小，泡の持続性も悪く全般的に起泡性のきわめて少ないことが認められる。AGE 系ブロックポリマーでは側鎖アルキル基が長鎖のものほど起泡性がやや低くなる傾向にあるが，オクチル以上の長鎖基をもつ試料は水分散液であり，直接比較することに若干問題がある。

2.3.4　木綿に対する湿潤性

　測定は木綿キャンバス (No. 6) の半微量ジスク強制沈下法[10]により 40°C で行なった。測定結果を第 7 表に示す。ブロックポリマー型試料は，いずれも低分子量の標準試料に比べかなり湿潤性が劣り，特に側鎖アルキル基の大きい AGE 系ブロックポリマーほどその傾向がはなはだしい。

3.　結　　言

　本報で取り扱われたブロックコポリマーはいずれも疎水ベースおよび付加ポリオキシエチレンの重合度分布が明らかにされておらず，また各試料について不定重合度の副生ポリグリコール（特に酸化エチレン高度付加体ほど多量）を含んでいると思われる。これらの諸点を明確にしてポリマーの性質を論ずることは望ましいが，実験的な困難が多い。ポリグリコールの除去に関しては，すでに二，三の方法が指摘されており[11),12)]，著者もなお検討中であるが，本研究の場合に満足しうる方法（特に重合度の高いポリグリコールの除去）がない。しかし食塩水洗浄法[11)]によってある程度脱ポリグリコールされた試料および Carbowax ($P_n$: 27, 90) を最高 30% まで添加した試料について，原試料との性質の比較を試みたところ，多少の異同はあるが著しい変化は認められなかった。結局，本報では AGE ポリマーを疎水ベースとして，ほぼプロピレンオキサイド系に近い性質をもつブロックコポリマー型非イオン性活性剤の得られることを示し，これらの二，三の性質および疎水ベースの平均分子量，側鎖アルキル基の鎖長との関係について定性的な傾向を示した。

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# Studies on the Surface Active Derivatives of Glycidyl- and Glyceryl-Ethers

## II. Preparation of Nonionics of Block Copolymer Type from Alkyl Glycidyl Ethers

By Tsunehiko Kuwamura*

For the purpose of obtaining low-foamable nonionics, preparation of block copolymers having next general formula was investigated.

$$HO(CH_2CH_2O)_{\overline{x}}-(CHCH_2O)_{\overline{y}}-(CH_2CH_2O)_{\overline{z}}H$$
$$|$$
$$CH_2OR$$
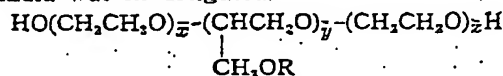
By polymerization of glycidyl alkyl(ethyl~dodecyl) ethers with alkali or acidic catalysts, the lower polymers ($P_n$: 4~30) (I) hydrophobic were obtained. Polyadditions of ethylene oxide to (I) of lower mol. wt. (<2500) gave easily soluble or dispersible in water, considerably surface active products (II). (II) are comparable to propylene oxide-ethylene oxide copolymer in the low foamability. When (I) are higher mol. wt. (>2500~3000) and contain longer alkyl side chain(amyl~dodecyl), solubility and surface activity of the obtained products (III) are generally poor, irrespectively contents of polyoxyethylene. However, (III) remarkably swell in water.

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[37] STUDIES ON SURFACE ACTIVE AGENTS COMPRISING GLYCIDYL ETHER

AND GLYCERIL ETHER AS INTERMEDIATES

II SYNTHESIS OF BLOCK POLYMER TYPE NONIONIC SURFACE ACTIVE

AGENTS FROM ALKYLGLYCIDYL ETHERS

By Tsunehiko KAWAMURA

Date of acceptance: Oct. 19, 1959

Abstract: $C_{2-12}$ alkylglycidyl ethers were polymerized by alkali or acidic catalysts to obtain lower polymers with an average polymerization degree of 4 to 30. In order to obtain low-foaming nonionic active agents, successive addition of ethylene oxide to these lower polymers was carried out to synthesize block polymers mainly comprising polyglycidyl ethers having the following formula as hydrophobic bases: $HO(CH_2CH_2)_y$-$[CH(CH_2OR)CH_2O]_z$-$(CH_2CH_2O)_zH$. Among block polymers having polyoxyethylene contents of 55% or higher, those which contain hydrophobic bases with molecular weights of 2,500 or lower and consisting of relatively short chains of the side chain alkyls were, in general, well dissolved or dispersed in water and had considerably high surface tension-lowering capability and showed foamability as low as that of propylene oxide-ethylene oxide-based active agents. In the case of hydrophobic bases consisting of long alkyl chains and having molecular weight of 2,500 to 3,000 or higher, even ethylene oxide additive polymers

were insufficient in the water-solubility as well as surface active properties, however, they were remarkably swollen in water.

## 1. Introduction

With respect to block polymer type nonionic active agents, Vaughn, et al., have already reported studies[1] on products comprising polypropylene oxide as a hydrophobic base and polyoxyethylene as a hydrophilic group and as innovative active agents with low formability, such products have been commercialized. Furukawa, et al.[2], have reported that although water-soluble block polymers were obtained from phenyl glycidyl ether polymers and ethylene oxide, they were poor in the surface activity. So far, derivatives from alkylglycidyl ethers (hereinafter, abbreviated as AGE) have not been reported yet. Separately from the studies by Vaughn, et al., based on investigations on polymerization of epoxy compounds performed before, the author found that polymers of ethylGE are water-insoluble even though they have low polymerization degrees and give water-soluble substances with relatively high surface activity by successively adding ethylene oxide thereto and that AGE polymers can be used as hydrophobic bases of surface active agents.

On the other hand, although AGE is scarcely produced and utilized industrially presently, it can relatively easily be obtained from aliphatic alcohols and epichlorohydrine and its applications may be wide as described in the previous report[3].

2

Here, in a series of studies on use application of AGE to active agents, in order to find the relations of the structure (particularly, the polymerization degree of a hydrophobic group-based main chain, the alkyl side chain length) of block polymers derived from AGE and a variety of properties, it has been tried to polymerize several kinds of AGE and obtain ethylene oxide adducts from them and their water-solubility and surface activity are roughly investigated.

2. Experiments and Results

2.1 AGE polymerization

AGE used for polymerization were all synthesized by the method described in the previous report[3] and their types and properties are shown in Table 1.

Table 1 Properties of raw material alkylglycidyl ethers

| ROCH2-CH-CH2 $\diagdown$o$\diagup$ R | Boiling point (°C/mmHg) | Oxirane-oxygen content(%)[*1] | | Specific gravity $d_4^{30}$ | Reflective index $n_{\eta}^{30}$ |
|---|---|---|---|---|---|
| | | Actual measurement | Calculation | | |
| C$_2$H$_5$- | 126.5 ~ 127.5 | 15.3 | 15.6 | 0.9302 | 1.4035 |
| n-C$_4$H$_9$- | 74 ~ 75/26 | 12.1 | 12.3 | 0.9041 | 1.4198 |
| i-C$_5$H$_{11}$- | 72 ~ 73/14 | 10.9 | 11.1 | 0.8987 | 1.4200 |
| 2-ethylhexyl | 89.5 ~ 90.5/2 | 8.38 | 8.51 | 0.8862 | 1.4305 |
| n-C$_8$H$_{17}$- | 140 ~ 141.5/30 | 8.45 | 8.51 | 0.8787 | 1.4301 |
| n-C$_{12}$H$_{25}$-[*2] | 119 ~ 120/1.2 | 6.44 | 6.61 | 0.8688 | 1.4391 |

*1 Ether-HCl method/glacial acetic acid-HBr method were employed (reference to the previous report)

*2 melting point 11.8°C to 12.3°C (corrected value)

Although there are reports 2), 4) of phenylGE, no report AGE cannot be found, the synthesis was carried out as follows using alkaline catalysts and acidic catalysts such as dehydrated tin tetrachloride, boron trifluoride, which are commonly used for polymerization of epoxy compounds.

2.1.1 Polymerization by alkaline catalyst

a. Normal pressure/no-stirring method:

4

A monomer mixed with 2 to 5% KOH powder was heated in a flask equipped with a refluxing cooling apparatus and moisture-prevention tube in an oil bath. Intense reaction was caused around 100°C and being accompanied with considerable reaction heat generation, the contents were turned to be yellowish brown or blackish brown and became viscous. Further, heating was continued for a long time to complete the reaction when no viscosity increase was observed. In this method, especially in case that the purity of the raw materials was high, the temperature at the time of starting the reaction was difficult to control.

b. Normal pressure/titration/stirring method

A small amount (1/5 or less of the total amount to be used) of a monomer and KOH powder were put in a three-mouth flask equipped with a moisture-prevention tube, a stirrer, a titration funnel, and a thermometer and gradually heated while being stirred. When heat generation starts, a heating bath was removed and the rest of the monomer is considerably gradually dropwise added (for about 1 hour or longer) and the content temperature was kept constant. By the method, temperature was controllable for long chains or butyl or higher.

c. Sealed tube method

A monomer and a catalyst were put in a sealed tube and heated in an oil bath for a long duration at a constant temperature and periodically fiercely shaken to disperse the precipitated catalyst.

Polymers obtained by the above-mentioned alkaline

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catalyst methods all showed blackish brown, however, they were turned to be pale yellow or pale blown with extremely slight loss (2% or less) by decoloration reciprocally using activated kaolin and activated carbon in a benzene solution alternately. The average polymerization degrees of the refined polymers were measured by a freezing point depression method (in benzene), Rast method, and an OH% measurement method[5], these methods showed generally the same results. The above results are shown in Table 2.

Table 2    Polymerization of AGE by basic catalyst

| Monomer R | Polymerization condition | | | | | | Refined polymer | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Catalyst | | | Heating temperature (°C) | Heating duration (hr) | Yield (%) | average molecular weight measured value (polymerization degree) | Measurement method * | Remarks | Sythesis No |
| | Method | Type | used amount (%) | | | | | | | |
| C2H5- | (a) | KOH powder | 5 | 110~140 | 30 | 85 | 805(8) / 815(8) | R / F | pale yellow and highly viscous liquid | E-8B |
| | | Triethylamine | 3 | 80~140 | 50 | – | – | – | no polymer obtained | – |
| n-C4H9- | (b) | KOH powder | 5 | 120~140 / 150~160 | 6 / 15 | 75 | 820(6.3) | R | pale brown and highly viscous liquid | B-6B |
| n-C4H9- | | KOH powder | 5 | 140~150 (dropwise) / 150~180 stirred 10 | 0.5 / 10 | 86 | 788(4.2) | R | pale orange brown and highly viscous liquid | B-4B |
| n-C8H17- | | KOH powder | 5 | 140~145 (dropwise) / 150~160 stirred 12 | 1 / 12 | 88 | 1323(7.1) | R | pale brown and highly viscous liquid | O-7B |
| n-C13H25- | | KOH powder | 5 | 160~165 (dropwise) / 165~175 stirred 7 | 1 / 7 | 85 | 850(3.5) | R | pale yellow wax melting point of 16°C to 18°C | D-3.5B |
| | (c) | KOH powder | 3.3 | 60~65 | 120 | 80 | 1960(19) | R | Brown and highly viscous liquid | E-19B |
| | | KOH powder | 3 | 95~100 | 50 | 84 | 1330(13) | R | Brown and highly viscous liquid | E-13B |
| | | KOH powder | 3 | 120~130 | 26 | 90 | 1110(11) | R | blackish color and highly viscous liquid | E-11B |
| C3H5- | | Triethylamine | 3 | 100~120 | 50 | – | – | – | no polymerization even after being kept for at least 1 year | – |
| | | KOH powder | 5 | 60~65 | 120 | 85 | 2800(22) | F | pale yellow and highly viscous liquid | B-22B |
| | | KOH powder | 5 | 95~100 | 50 | 79 | 3030(23) | F | pale orange and highly viscous liquid | B-23B |
| | | KOH powder | 10 | 95~100 | 50 | 88 | 4010(31) / 4350(33) | F / OH | pale brown and highly viscous liquid | B-31B |
| n-C4H9- | | KOH powder | 5 | 120~130 | 25 | 84 | 2200(17) | F | blackish color and highly viscous liquid | B-17B |
| i-C5H11- | | KOH powder | 5 | 57~60 | 150 | 93 | 2880(20) | F | pale yellow and highly viscous liquid | A-20B |
| 2-ethylhexyl | | KOH powder | 1 | 120~130 | 200 | – | – | – | no polymerization even after being kept for at least 6 | – |
| n-C8H17- | | KOH powder | 1 | 120~130 | 100 | 94 | 4600(25) | R | pale brown and highly viscous liquid | O-25B |
| n-C12H25- | | KOH powder | 1 | 120~130 | 100 | 90 | 2660(11) / 2710(11) | R / OH | pale yellow wax melting point of 22.5°C to 24.5°C | D-11B |

* : Rast method ; F: freezing point depression method (solvent; benzene), OH : OH% measurement method

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Main experiment results of the Table are as follows: (1) tertiary amine base such as triethylamine was not found having a catalytic effect and in this point, it is different from the case of ethylene oxide polymerization: (2) to obtain polymers with low polymerization degrees, reactions under normal pressure were suitable and particularly, the method (b) gives low polymers at high yield in a short time by polymerization at relatively high temperatures: (3) the sealed tube method was suitable for obtaining polymers with relatively high polymerization degrees and in such cases, it took longer time as the reaction temperature was lower, however higher polymers could be obtained: (4) in general, difference in polymerization depending on the length of the alkyl group was not significantly observed, however, only in the case of 2-ethylhexyl monomer, the monomer was recovered quantitatively any time although the sealed tube polymerization was carried out three times using the fresh KOH powder catalyst: and (5) in general, it took long time for polymerization using the KOH powder catalyst, however, proper selection of the polymerization conditions made it possible to obtain polymers with average polymerization degrees of 4 to 30 from various monomers at high yields.

2.1.2 Polymerization by acidic catalyst

a. A monomer was put in a test tube equipped with a moisture prevention tube and cooled to 0°C or lower. Small amount of dehydrated ligroin containing 1 to 10% of dehydrated tin tetrachloride was further added and the mixture was kept still.

b. A monomer, a dehydrated solvent with the same amount or more

of that of the monomer, and an ampoule enclosing a catalyst in an amount of 1 to 5% to the monomer were put in a three-mouth flask equipped with a thermometer, a titration funnel, a moisture prevention tube, and a stirrer and the stirrer was rotated so as to break the ampoule and disperse the catalyst. The contents were cooled to –10°C to -50°C and then added dropwise while the temperature of the monomer being carefully kept at 5°C or lower. After that, the mixture was continuously stirred for a while around 0°C.

c. A catalyst solvent was added to a monomer at approximately same ratio as that in the case of a. and heated in a sealed tube to 80°C to 100°C.

The products obtained by these methods were dissolved in ethers and shaken with an aqueous high concentration (10% or higher) of NaOH solution to decompose the catalysts (if a low concentration alkali was used, emulsification took place to make ether layer separation difficult) and two-liquid-phase layers were separated. The ether layers were washed with water and dried, then the solvent was removed by distillation to obtain polymers. The reaction results are shown in Table 3 in a lump.

Table 3    Polymerization of AGE by acidic catalyst

| Monomer R | Method | Catalyst Type | Catalyst used amount (g) *1 | Type | used amount (g) | Temperature (°C) | duration (hr) | Yield (%) | Average molecular weight measured value (polymerization degree) | Measurement method *3 | Remarks | Synthesis No |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| n-C4H9- | (a) | SnCl4 | 0.02 | ligroine | 1 | 0~10 | 10 | <5 | - | - | - | - |
| C2H5- | | SnCl4 | 1.1ℓ | petroleum ether | 40 | -2~5 | 4 | 59 | 650(6.4) | F | colorless and viscous liquid | E-6A |
| n-C4H9- | (b) | SnCl4 | 0.75 | ligroine | 30 | -2~4 | 3.5 | 81 | 780(6.0) 1020(8.0) | R OH | colorless and viscous liquid | B-6A |
| | | BF3(C3H5)2O*2 | 0.25 | petroleum ether | 30 | -10~-5 | 6 | 50 | 1080(8) 1870(14) | F OH | colorless and viscous liquid | B-8A |
| n-C8H17- | | SnCl4 | 1.2ℓ | ligroine | 40 | 0~3 | 5 | 77 | 1310(7) | R | pale yellow and viscous liquid | O-7A |
| iso-C8H17- | (c) | SnCl4 | 0.15 | ligroine | 5 | 80~100 | 20 | 32 | 560(3) | R | pale yelloq and highly viscous liquid | O-3A |
| n-C12H25- | | SnCl4 | 0.15 | ligroine | 5 | 80~100 | 20 | 40 | 1005(4) | R | pale yellow wax melting point of 17°C to 19°C | D-4A |

*1 : the use amount per 25g of each monomer

*2 : Product manufactured by Eastman Kodack was used after one time distillution, boiling point 124.5°C to 126°C

*3 : R : Rast method, F: freezing point depression method

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The experiment results are summarized as follows. According to these methods, although the yields and the polymerization degrees were relatively low in general as compared with those in the case of alkaline catalyst methods, coloration of the polymers was considerably scarce and decoloration process was not required. Further, the time took for the reactions was short. The average polymerization degrees of polymers obtained by using $BF_3(C_2H_5)_2O$ as a catalyst differed depending on the measurement methods and OH% methods give about 2-times as high as that of the freezing point depression method. It is supposedly attributed to a catalyst fragment (ethyl group) bonded to a polymer terminals[6]. Also in the case of using dehydrated tin tetrachloride as a catalyst, the measured values of the polymerization degrees by OH% measurement method tended to be high, however, the difference was not significant.

Polymers obtained by both catalyst methods were all water-insoluble and easily dissolved in benzene, pyridine, an ether, and dioxane and lower polymers or polymers with long chain alkyl groups were easy to be dissolved in an alcohol, acetone and the like, however, many of other polymers were hardly soluble when cooled. The viscosity of the polymers was generally high and seemed to have low temperature dependency. The viscosity of the polymers having higher side chain alkyl groups tended to be decreased slightly more at the same temperature.

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## 2.2. Ethylene oxide addition to AGE polymer

## 2.2.1 Reaction method and progress

The reaction method was an ethylene oxide blowing method[7] using a potassium hydroxide powder as a catalyst under normal pressure. Prior to the reaction, the apparatus was evacuated with $N_2$ gas or argon gas. In the case of AGE polymers with relatively low molecular weights, ethylene oxide absorption was smooth and prescribed reaction increase amount could be obtained in 4 to 8 hours. However, in the case of AGE polymers with high molecular weight or having long chain alkyl groups, generally the absorption was not smooth and in many cases, relatively long duration was required, supposedly attributed to low viscosity of the reaction systems and low concentration of the terminal hydroxyl groups.

## 2.2.2 reaction results (of mainly water-soluble products)

Besides polyAGE type block polymers, ethylene oxide addition to n-dodecanol and polypropylene oxide (product of Dow Chem. Co., colorless viscous liquid, MWn: 1,120) with high purity as comparative substances was carried out in the same manner to synthesize samples. The reaction results are shown in Table 4 in a lump.

Table 4    Ethylene oxide addition to polyglycidyl ether

| Synthesis No. | Hydrophobic base | | | Reaction condition | | | | Basic mole ratio [*2] EO/GE | Product | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Structure | Average molecular weight | n | Catalyst amount (%) | Temperature (°C) | time (hr) | ethylene oxide [*1] addition amount (%) | | appearance | water-solubility [*3] |
| S-12(61) | $H-(CH_2)_n-O-$ | 185 | 12 | 1 | 135~140 | 5 | 61 | 6.6 | pale yellow semi-solid | soluble in transparent state |
| P-20(55) | $(-CH-CH_3-O-)_n$ with $CH_3$ | | | 3 | 130~135 | 5 | 55 | 1.6 | pale gray semi-solid | soluble in transparent state |
| P-20(76) | | 1120 | 20 | 3 | 130~135 | 6 | 76 | 4.2 | pale brown wax | soluble in transparent state |
| E-8B(76) | $(-CH-CH_2O-)_n$ with $CH_2OC_6H_5$ | 810 | 8 | 3 | 130~135 | 4 | 76 | 7.1 | pale yellow semi-solid | soluble in transparent state |
| E-13B(59) | | 1330 | 13 | 2 | 135~140 | 6 | 59 | 3.3 | pale orange semi-solid | soluble in transparent state |
| B-6B(52) | $(-CH-CH_2-O-)_n$ with $CH_2O_n-C_4H_9$ | 820 | 6.3 | 3 | 120~130 | 10 | 52 | 3.2 | pale yellow semi-solid | opaque dispersion |
| B-6A(57) | | 780 | 6 | 2 | 130~135 | 12 | 57 | 4.0 | pale yellow semi-solid | thinly opaque and almost all dissolved |
| B-17B(63) | | 2220 | 17 | 5 | 140~150 | 8 | 63 | 5.0 | pale yellow viscous wax | opaque dispersion |
| A-20B(40) | $(-CH-CH_2-O-)_n$ with $CH_2O_i-C_5H_{11}$ | | | 2 | 135~140 | 9 | 40 | 2.2 | pale brown semi-solid | hardly soluble and slightly dispersed |
| A-20B(76) | | 2880 | 20 | 4 | 140~145 | 15 | 76 | 10.5 | pale gray wax | dispersed and slightly soluble |
| O-7A(64) | $(-CH-CH_2-O-)_n$ with $CH_2O_n-C_6H_{13}$ | 1310 | 7.0 | 2 | 130~135 | 17 | 64 | 7.5 | yellowish white wax | thinly opaque and dispersed |
| O-7B(71) | | 1323 | 7.1 | 1 | 150~160 | 8 | 71 | 10.3 | yellowish white wax | thinly opaque and dispersed |
| D-3.5B(54) | $(-CH-CH_2-O-)_n$ with $CH_2O_n-C_2H_5$ | | | 1 | 150~160 | 5 | 54 | 6.5 | pale brown viscous wax | opaque dispersion |
| D-3.5B(74) | | 850 | 3.5 | 1 | 150~160 | 6 | 74 | 15.7 | yellow wax | thinly opaque and dispersed |
| D-4A(74) | | 1005 | 4.0 | 2 | 135~140 | 10 | 74 | 15.7 | yellow wax | thinly opaque and dispersed |
| D-11B(42) | | | | 3 | 140~145 | 8 | 42 | 4.0 | white semi-solid | insoluble |
| D-11B(68) | | 2660 | 11 | 3 | 140~145 | 10 | 68 | 11.7 | yellowish white wax | hardly soluble and slightly dispersed |

*1: weight of ethylene oxide bonded in product measured by the amount increased by reaction.

*2: EO : ethylene oxide  GE : glycidyl ether

*3 : appearance when 0.5% of each product was dissolved in water.

Although it is not shown, according to the results of the molecular weight measurement of the products by numerical values, values generally higher than the raw material polymers and rather lower than the values calculated based on the reaction increase were obtained. Particularly, in the case of raw material polymers with high molecular weights, such tendency was significant and therefore, the amounts of byproducts such as polyglycols not bonded with the hydrophobic bases were supposed to be relatively higher than the cases of general nonionic active agents. However, no water-soluble or dispersible product could be obtained by simply mixing and heating AGE polymers and polyglycol. The reaction products were supposed to be, as expected, polymers of mainly containing at least block polymers bonded with polyglycol chains to a certain extent. The results of Table 4 can be summarized as follows: (1) in the case of 2,000 or lower molecular weight of a hydrophobic base and 55 to 60% ethylene oxide addition amount, common water-soluble or highly dispersible products could be obtained, however, if the hydrophobic base had a high molecular weight, even a high ethylene oxide addition product was scarcely dispersible or hardly soluble. However, as A-20B (40) shown in Table, even the hardly-soluble product obtained by addition of ethylene oxide to the polymer hydrophobic base to a low addition degree had a property of being swollen gradually in water and it shows a possibility of its application to a protection colloid for emulsion dispersion depending on the conditions: (2) also, with respect to an ethylene oxide addition

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product of hydrophobic base with a molecular weight of 2,000 or lower and approximately the same ethylene oxide addition degree, those having longer alkyl groups as the side chains tended to show decreased water-solubility showing that the hydrophobic property of the AGE polymers considerably depended on not only the polymerization degree but also the alkyl chain length. Accordingly, the water-solubility of these block polymers was supposedly regulated by the molecular weight, the alkyl chain length, and the ethylene oxide chain length rather than the hydrophobic base polymerization degree: and (3) in the case of polymerization of raw material polymers, the water-solubility of the final products was not so affected by whether an alkaline or acidic catalyst was used.

2.3 Property of aqueous block polymer solution

2.3.1 Cloud point and viscosity

Water-soluble products showed relatively sharp cloud points just like common nonionic active agents. Some measured value examples are shown in Table 5.

Table 5 Cloud point of aqueous block polymer solution

| Concentration(%) | Cloud point (°C) | | |
|---|---|---|---|
| Synthesis No. | 3 | 1 | 0.5 |
| S−12 (61) | 46.8 | 48,0 | 49.7 |
| P−20 (55) | 77.1 | 76.0 | 75.4 |
| E−8B (76) | 86.2 | 83.8 | — |
| E−13B (59) | 94.1 | 94.2 | 95.2 |

There was no regular relation of the cloud points with the concentrations or estimated HLB values and in the case of a block polymer type nonionic active agent, distributions of the hydrophilic group length and the polymerization degree of a hydrophobic base were observed and besides, the amount of polyglycol, a byproduct, was high and therefore, the production amount was not stabilized and in such a manner, the factors relevant to the cloud point were extremely complicated to make

it difficult to use the cloud point as a characteristic value.

With respect to some samples dissolved in transparent state in water, the viscosities of aqueous diluted solutions with 5 g/100 cc or lower concentration were measured in a thermostat at 25 $\pm$ 0.05°C using an Ostwald viscometer (flow down duration of distilled water 200 to 300 sec). The relation between the concentration and the Reduced Viscosity ($\eta$/C) is shown in Fig. 1.

Since the purities of samples were unclear, I should refrain from discussions stepped in too far, however, the measurement results made it clear as follows: the viscosity behavior of a common nonionic active agent (having a long chain hydrophilic group only in one terminal of a hydrophobic group) just like S-12(61) in a low concentration range of 0.5 g/100 cc or lower was different from that of a block polymer. That is, in the relation curve of the former was supposed to have the maximum value probably in the concentration of 0.1 g/100 cc or lower (in this concentration or lower, the measurement precision is doubtful and therefore it is not illustrated), meanwhile such a tendency could not be observed in the curve of the latter. However, both had clear flexal points in certain concentrations in the range of 1.0 g/100 cc or lower and the concentration at the flexal points were approximately corresponding to the flexal points of the surface tension-

concentration curves shown below, and therefore, the viscosity behavior of an aqueous solution of a block polymer type active agent was supposed to be relevant to the production of a micellar agglomerates and the agglomerate formation was assumed to be in the form of a string ball-like shape similar to the random coil from the initial stage of the production as compared with the common nonionic active agent (S-12(61)). In the concentration in the side higher than the flexal point, the specific viscosity seemed to depend on mainly the magnitude of the molecular weight of a hydrophobic base.

2.3.2 Surface tension

Using a Du Nouy type tensiometer, the surface tension was measured at temperatures of 27°C to 29°C. At first, the comparison between a standard type sample and a representative example (E-13B(59) of AGE-type block polymers was shown in Fig. 2.

As compared with that of a polyglycol monoalkyl ether such as S-12(61), the surface tension decrease of a block polymer type active agent was slightly low, however, in the case of AGE polymers, the surface tension decrease was better than that of propylene oxide polymers and particularly, since the flexal

point in the surface tension-concentration curve, that is, assumed cmc concentration was low, the rather high surface activity was shown with a relatively low concentration.

Fig. 3 shows the comparison of samples of AGE block polymers comprising hydrophobic bases with molecular weight of 2000 or lower (soluble or highly dispersible products) and having different length of the alkyl chains as side chains among AGE block polymers.

Although not so significant difference was observed among those comprising alkyl groups from ethyl to dodecyl as side chains, those comprising longer alkyl chain length tended to be slightly excellent in the surface tension-decreasing capability.

Next, the effect of the molecular weight of a hydrophobic base on the surface activity of a block polymer is shown in Fig. 4.

Samples used were poor in water-solubility and could be subjected to the measurement only with extremely low

concentration, however, it could be said that the excessive increase (2,500 or higher) in the molecular weight of the hydrophobic base considerably decreased the surface activity. Based on the investigations on the difference in the surface activities of monomers and polymers with respect to allyl ester salts of α-sulfofatty acids, Bistline[8], et al., confirmed that polymers (polymerization degrees about /0 ) were considerably inferior in the surface tension decreasing-capability, swelling property, and washing power but relatively excellent in the emulsification and dispersion capability. The types of those active agents are slightly different from those of the block polymers of this study and it is therefore controversial to make discussions from the same viewpoint, however, these results are supposed to imply that even with respect to soluble active agents, if hydrophilic-Lyophilic balance is well kept, the molecular weights of compounds having significant surface activity are limited and if molecular weights are beyond the limit, the properties of such compounds may be shifted to the properties like polymer-protection colloids.

2.3.2 Foamability

Using a 0.6 L Stay bell        type flask, 40 cc of each sample liquid was shaken to carry out foaming under the following conditions, and the foaming surface and the liquild surface were observed: temperature: $30 \pm 1°C$, sample concentration: 0.25, 0.05%, after kept for 15 minutes in a thermostat, the flask containing the sample liquid was taken out and shaken up and down 100 times for 1 minute and turned

back to the thermostat and that time was set to be time 0. The foaming surface and the liquid surface were read after 1, 3, 5, and 10 minutes.

Display of the results: according to the handling[9] of Nakagawa, the measurement results were processed. The results are shown in Table 6.

Foaming coefficient (FC) = foaming volume × foaming liquid amount

Specific foaming volume (FV) = foaming volume/foaming liquid amount

Deforming ratio $(DFC_t)$ = $(FC_1 - FC_t)100/FC_t$.

Table 6 Foamability of aqueous block polymer solution

| Concentration (%) Sample | 0.25 | | | | 0.05 | | | |
|---|---|---|---|---|---|---|---|---|
| | $FC_1(a)$[*1] | $FV_3$ | $DFC_3$ | $DFC_{10}$ | $FC_1(a)$[*1] | $FV_3$ | $DFC_3$ | $DFC_{10}$ |
| $n\text{-}C_{12}H_{25}OSO_3Na\text{-}$[*2] | 1265 (186) | 88 | 52 | 80 | 145 (35) | 13 | 44 | 75 |
| Igebon T[*3] | 3030 (416) | 274 | 45 | 76 | 700 (70) | 34 | 61 | 78 |
| S-12 (61) | 2340 (233) | 110 | 58 | 80 | 539 (62) | 17 | 55 | 72 |
| P-20 (55) | 66 (32) | 14 | 80 | 98 | 3 (5) | 8 | 77 | 99 |
| E-13B (59) | 102 (47) | 21 | 48 | 88 | 65 (16) | 16 | 74 | 95 |
| B-6A (57) | 120 (54) | 22 | 62 | 92 | 43 (12) | 12 | 61 | 90 |
| O-7A (64) | 43 (18) | 15 | 75 | 94 | 5 (5) | 11 | 52 | 83 |
| D-4A (74) | 8 (6) | 6 | 40 | 76 | 3 (4) | 8 | 58 | 82 |

*1 (a) the number value in the parentheses shows the actual foaming volume (cc)
*2 purely synthesized sample
*3 commercialized product

It was confirmed that block polymer type samples all had considerably low foaming coefficients, relatively low specific foaming volumes, inferior sustainability of the foams as compared with other common standard type active agents and as a whole, they has scarce foamability. On the other hand, with respect to the AGE type block polymers, although those having long length of alkyl chains as side chains tended to have slightly low foamability, samples with long chains of octyl or higher alkyl groups were dispersible in water and therefore, the direct comparison between both types of the samples is more or less controversial.

2.3.4 Swelling property to cotton

Measurement was carried out at 40°C by a half-amount disk-forced precipitation method[10] of cotton canvas (No. 6). The measurement results are shown in Table 7. The block polymer type samples were found all inferior in the swelling property as compared with the standard sample with a low molecular weight and particularly the AGE type block polymers with higher alkyl groups as side chains showed such tendency more considerably.

Table 7 Swelling force (40°C) of block polymer

| Sample | Precipitation time (sec) | | | | |
|---|---|---|---|---|---|
| | 0.5% | 0.25% | 0.1% | 0.05% | 0.025 |
| n-$C_{12}H_{25}OSO_3Na$- | 5.3 | 8.6 | 36.2 | 126 | Not precipitated* |
| S-12 (61) | 4.0 | 5.2 | 13.2 | 25.2 | 73.5 |
| P-20 (55) | 28 | 87 | 315 | Not precipitated* | — |
| E-8 B (76) | 144 | 354 | Not precipitated* | — | — |
| E-13 B (59) | 31.4 | 74,0 | 221 | Not precipitated* | — |
| B-6A (57) | 460 | Not precipitated* | — | — | — |
| O-7A (64) | 840 | Not precipitated* | — | — | — |
| D-4A (74) | Not precipitated* | — | — | — | — |

* Those which were not precipitated in 20 minutes.

## 3. Conclusion

With respect to all of the block polymers described in this report, the polymerization degree distribution of the hydrophobic bases and added polyoxyethylenes was not made clear and further, the respective samples were supposed to contain the polyglycols (particularly ethylene oxide adducts to a higher extent contain more), byproducts with not-specified polymerization degree. It is desirable to make discussion on the polymer properties while making such points clear, however, it is accompanied with experimental difficulty. With respect to removal of the polyglycols, some methods have been reported already[11], [12] and the author has been investigating and has not found any method satisfactory for the cases of the study (particularly a method for removing polyglycols with high polymerization degrees) yet. However, when properties of the samples from which polyglycols were removed to a certain extent by a salt water washing method[11] and to which Carbowax (Pη: 27, 90) was added up to 30% were compared with those of their raw materials, there were more or less changes, however, the changes were not so significantly observed. As a conclusion, this report describes that block copolymer type nonionic active agents having properties approximately similar to those of polypropylene oxide type ones can be obtained using AGE polymers as hydrophobic bases and describes the qualitative tendency with respect to the some properties of the active agents and the correlations with the average molecular weights of the hydrophobic bases and the length of the alkyl side chains.

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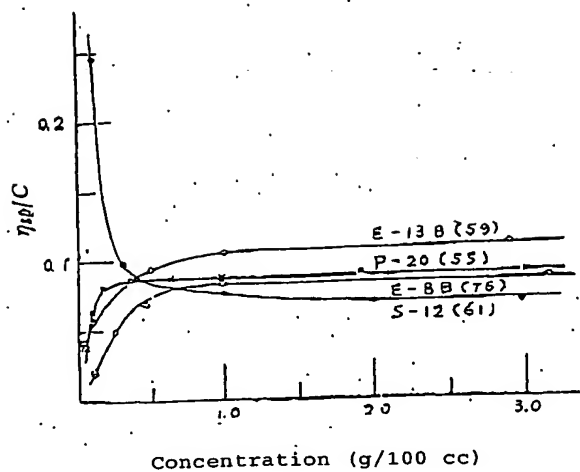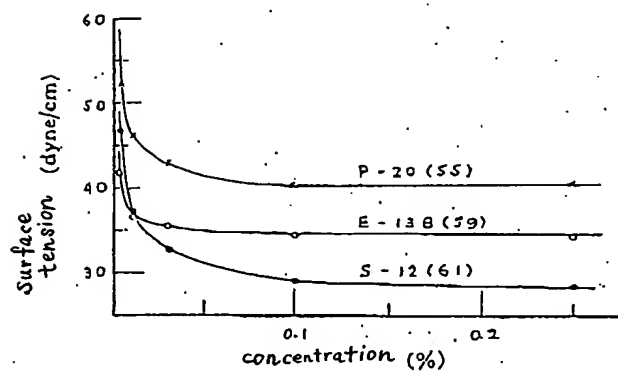
Fig. 1 Viscosity of aqueous diluted solution of block polymer
(25 ± 0.05°C)



comparison between AGE-type block polymers and standard type

nonionic active agent

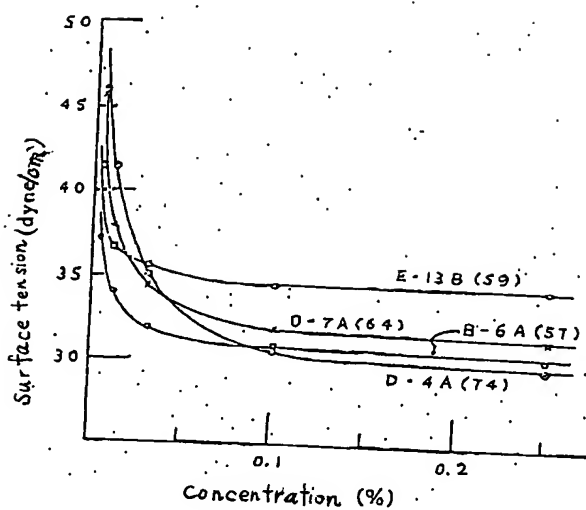Fig. 2 Surface tension-concentration curve (27°C to 29°C)

Fig. 3 Surface tension-concentration curve (27°C to 29°C) of soluble block polymers with different length of alkyl chains as side chains
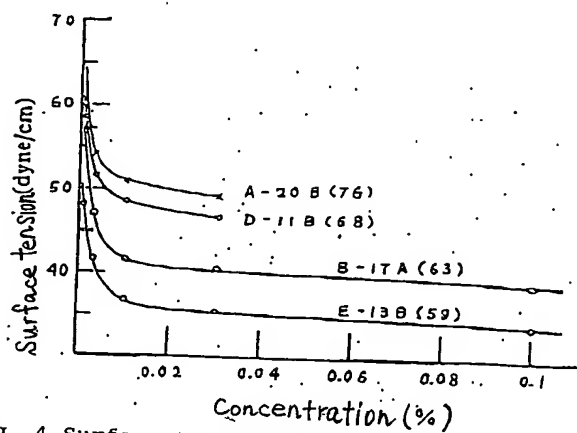


Fig. 4 Surface tension-concentration curve (27°C to 29°C) of block polymers comprising hydrophobic bases with high molecular weights